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Annual Report covering the period
August 1, 1988 - June 30, 1989

SRI International
333 Ravenswood Avenue
Menlo Park, CA 94025-3493

PROCESSING AND FABRICATION OF HIGH
TEMPERATURE OXIDE SUPERCONDUCTORS

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FIELD	GROUP	SUB-GROUP										
20	03											
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19. ABSTRACT (Continue on reverse if necessary and identify by block number) During the past year, we have been optimizing a process for synthesizing superconductor powders by freeze-drying. Our objectives are to develop an understanding of the processing of these powders and to fabricate simple shapes from freeze-dried powders. We have synthesized a series of powders from solutions of barium acetate, copper nitrate, and yttrium nitrate, with pH values of 2.8 to 9.8 and calcined at temperatures from 510° to 908°C. We are determining the surface area of these powders by BET and XRD. Selected powders are being characterized by SEM, DTA, ICP analysis (performed at Stanford University), carbon analysis, and tap density. The highest surface area (in lightly milled powders) of 4.4 m^2/g ² was achieved with a pH of 4 in a series of experiments in which the Ba and Y solutions were mixed together before the Cu nitrate solution was added, then calcined at 825°C. Surface areas decrease with increasing calcining temperature, however. It appears that calcining at 750° or												
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Item 19. Abstract (Concluded)

850°C gives the best critical temperature, with complete transitions at greater than 90K. Critical temperature measurements performed at Stanford show that we have achieved our goal of a critical temperature of $T_c > 90K$ and a temperature difference, W, between 10% and 90% of transition of <2K.

We have delivered 150 g of powder to Ceracon. Now that we have received the larger freeze-dryer, we will be producing larger quantities of powder for other contractors. We will continue our investigation of the effects of calcining and freeze-drying on powder characteristics, including efforts to decrease agglomeration, improve reproducibility of T_c , and decrease W. We will also begin investigating reproducibility in large batches and fabrication of simple shapes from powders.

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Program Summary

The objectives of this program are to understand and optimize the synthesis of superconductor powders by freeze-drying, to develop an understanding of the processing of these powders, and to fabricate simple shapes from freeze-dried powders.

Program Status

The program began on August 1, 1988. The milestones established for the quarter ending June 30, 1989, and our progress on these milestones are summarized below.

- Continue investigation of the stoichiometry/composition problem.

We are continuing to use the methods described in the previous report. In addition, we are performing DTA and other analyses to characterize the powders better.

- Investigate calcining and freeze-drying effects on powder characteristics.

A series of powders was calcined at various temperatures, and the effects of calcining temperature on the T_c of the sintered samples were determined. Other characterization of these materials is being performed by SEM, particle size analysis, DTA, and carbon analysis. This work is continuing.

- Investigate and decrease agglomeration.

We have investigated the effects of breaking up the frozen platelets formed on spraying by blending the mixture before drying.

- Supply better powders to Ceracon and others.

We have been unable to supply large quantities of powders because of lack of freeze-drying capacity. However, now that the new freeze-dryer has been received, this situation will be resolved.

- Improve reproducibility.

So far, we have concentrated on determining the effects of synthesis variables. We will address reproducibility during the next quarter using the larger freeze-dryer.

- Improve T_c values ($T_c > 90K$ and $W < 2K$).

The latest powders have T_c values $> 90K$. Most transitions are sharp and $< 2K$.

Accomplishments

Our accomplishments from the beginning of the program to date are summarized below.

Supply of Powder to Ceracon. We supplied ~150g of powder to Ceracon for use in its densification process. Half of this powder was calcined at 825°C and half was calcined at 890°C. We are not supplying powder to others until we can produce larger quantities of high quality powder.

Evaluation of Effects of Synthesis Variables. We investigated the effects of pH, order of addition of various salts, and the role of starting materials early in the program. Recently, we investigated the effects of the calcining temperature on various powder and material properties. Table 1 summarizes the effects of various synthesis variables on some powder properties. Analysis of our materials indicated a stoichiometry problem, and our approach to the solution of this problem is described in a later section.

Originally we used solutions of Ba acetate, Cu nitrate, and Y nitrate--all prepared from the salts. Observation of the amount of precipitation and measurement of the surface area of powders indicated that the highest surface areas were obtained when the Ba and Y solutions were mixed together before the Cu nitrate solution was added. The highest surface area of $4.4 \text{ m}^2/\text{g}$ was achieved with a pH of 4 in this series of experiments.

Copper nitrate solutions are now being prepared by dissolving Cu in nitric acid. Later experiments with Cu nitrate solutions prepared from Cu metal indicate that a higher pH, about 4.6, results in a powder with a surface area $>4 \text{ m}^2/\text{g}$, which can be dried to a dry fluffy powder using an initial temperature of -35°C as opposed to -50°C. This higher temperature is an improvement because previously only specially equipped freeze-dryers could be used for this process. The yield of powder from one run in our small freeze-dryer was also improved to ~175 g from 150 g.

A series of powders was calcined at temperatures ranging from 510° to 908°C. The surface areas of the powders and T_c data on sintered materials are given in Table 2. Sintered densities are usually in excess of 95% of theoretical density. Surface areas decrease with increasing calcining temperature as expected. It appears from these results that calcining at 750° or 850°C gives the best T_c data, with complete transitions $>90\text{K}$. It is unclear why there should be two maxima in this relationship, and the experiments are being repeated.

TABLE 1
EFFECTS OF SYNTHESIS METHODS ON SUPERCONDUCTING POWDERS

Powder	Method	pH	Calcine Temp. (°C)	BET (m ² /g)	Typical Sample T _c (ρ=0; K) ^d	X R D Information ^c
DP1-8	Nitrates + Ba(Ac)	4.02	825	4.35		CuO
DP2a-43	Ba(Ac)+Nitrates(Y then Cu)	3.75	825	3.67		CuO;Y ₂ O ₃
DP2b-43	Ba(Ac)+Nitrates(Y then Cu)	8.79	825	3.15		CuO;Y ₂ O ₃
DP2c-43	Ba(Ac)+Nitrates(Y then Cu)	3.78	825	4.35		CuO;Y ₂ O ₃
DP3a-43	Ba(Ac)+ Nitrates(Cu then Y)	3.64	825			
DP3b-43	Ba(Ac)+ Nitrates(Cu then Y)	8.63	825			
DP3c-43	Ba(Ac)+ Nitrates(Cu then Y)	3.95	825			
DP4a-43	Nitrates(Y then Cu)+Ba(Ac)	3.73	825			
DP4b-43	Nitrates(Y then Cu)+Ba(Ac)	8.67	825			
DP4c-43	Nitrates(Y then Cu)+Ba(Ac)	4.06	825	3.98		
DP5-48	Ba(Ac)+Nitrates(Y then Cu)	3.41	825	3.03		
DP6a-48	Ba(Ac)+Nitrates(Cu then Y)	9.77	825			
DP6b-48	Ba(Ac)+Nitrates(Cu then Y)	3.51	825			
DP7-48	Nitrates(Y then Cu)+Ba(Ac)	3.53	825	3.21		
DP8-67	Ba(Ac)+Nitrates(Y then Cu)	3.86	825	3.59	80	CuO;Y ₂ O ₃
DP9-20	(Cu°+HNO ₃)+Ba+Y	3.87	830	4.09	82	
DP10-12	Ba(Ac)+Nitrates(Y then Cu)	4.00	810	4.04	68	2-1-1 phase
DP11-20	(Cu°+HNO ₃)+Ba+Y	4.00	827	1.66		
DP12-14	(Cu°+HNO ₃)+Ba+Y	4.63	825	4.24		
DP13-12	(Cu°+HNO ₃)+Ba+Y ^a	4.53	825			
DP13-12MQ	(Cu°+HNO ₃)+Ba+Y ^a		890	0.82	62	
DP14-12	(Cu°+HNO ₃)+Ba+Y ^a	4.23	825	1.29	65	BaCO ₃ ; 2-1-1; CuO
DP15-84	(Cu°+HNO ₃)+Ba+Y ^a	4.14	825	1.68	71	BaCO ₃ ; 2-1-1; CuO

^aMixing of 3 separate stock solutions.

^bSeparate Cu & Y Solutions; Ba added last in powder form.

^cExtra phases present in small percentages of ~2% or less.

^dT_c measurements from bulk samples sintered at 890°C.

TABLE 1 (concluded)

EFFECTS OF SYNTHESIS METHODS ON SUPERCONDUCTING POWDERS

Powder	Method	pH	Calcine Temp. (°C)	BET (m ² /g)	Typical Sample T _c (ρ=0; K) ^d	X R D Information ^c
DP16	(Cu ^o +HNO ₃)+Ba+Y ^a	4.08	-			
DP17-42	(Cu ^o +HNO ₃)+Ba+Y ^b	4.03	825	2.19	87	Clean 1-2-3
DP17-42MQM	(Cu ^o +HNO ₃)+Ba+Y ^b	4.03	890	7.51		Clean 1-2-3
DP18-24	Acetates(Ba+Cu)+Y(Nitrate)	4.76	825	1.63	80	
DP19-18	(Cu ^o +HNO ₃)+Ba+Y ^b	4.52	825	-	79	
DP19-18	(Cu ^o +HNO ₃)+Ba+Y ^b	4.52	825	-	83	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	510	2.78	90	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	600	2.2		semicond.
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	650	4.49	86	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	700	3.13	86	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	750	1.57	91	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	800	1.76	75	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	825	2.33	80	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	835	2.17	84	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	853	1.17	92	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	868	1.15	80	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	875	2.04	-	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	895	0.29	80	
DP20-12	(Cu ^o +HNO ₃)+Ba+Y ^b	5.35	908	0.39	88	
DP21	(Cu ^o +HNO ₃)+Ba+Y ^b	2.85	-	-	-	
DP22	(Cu ^o +HNO ₃)+Ba+Y ^b	3.21	-	-	-	

^aMixing of 3 separate stock solutions.^bSeparate Cu & Y Solutions; Ba added lastly in powder form.^cExtra phases present in small percentages of ~2% or less.^dT_c measurements from bulk samples sintered at 890°C.

Table 2
EFFECT OF CALCINING TEMPERATURE ON SURFACE AREA AND T_c

Calcining Temperature (°C)	Surface Area		T_c^a (K)	W ^b (K)	$T_{\rho=0}^c$ (K)
	(BET)(m ² /g)				
650	4.5		90	6	86
700	3.1		91	6	86
750 ^d	1.6/2.4		92	2	91
800	1.8		85	12	75
825	2.3		89	10	80
853	1.2		93	5	92
868	1.2		91	15	88
895	-		89	10	80
908	0.4		90	4.5	86

^a T_c = temperature at midpoint of transition

^bW = temperature difference between 10% and 90% of transition.

^cTemperature at resistivity (ρ) = 0.

^dSee Figures 1 and 3.

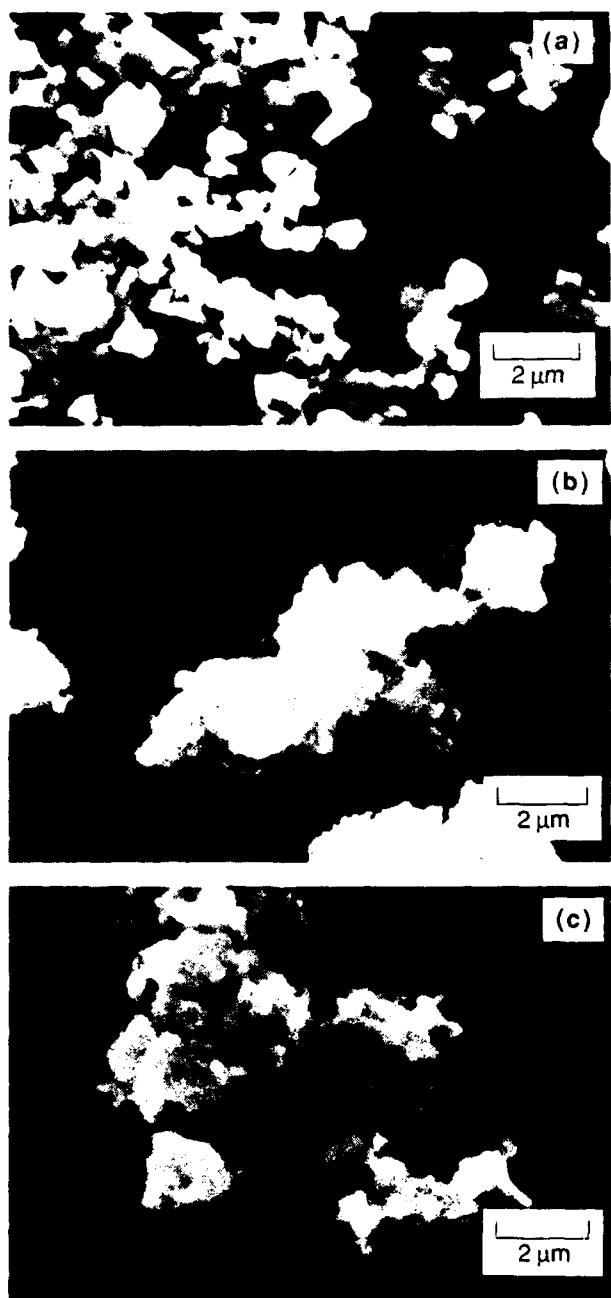
Currently, solutions are ultrasonically sprayed into liquid N₂ in shallow trays. This method results in the formation of platelets of frozen material, which result in agglomerated powders. We are exploring two approaches to solving this problem. In the first approach, the frozen material is "blended" in a commercial blender before drying. The surface area of blended material is 2.5 m²/g compared to 2 m²/g for unblended material. The second approach, which will be investigated during the next quarter, is to prevent the formation of the platelets by spraying into larger containers and stirring.

The combination of nitrates and acetates present in our mixtures can be explosive, particularly if there is insufficient gas flow to remove the volatile products. The calcination must begin about 150°C to prevent rehydration and melting of the mixture; however, the higher the initial temperature the greater the chance of the powder exploding. Lowering the initial temperature from ~300°C as used in the early work to ~150°C in the more recent work minimizes the explosion risk and reduces the intensity of the accompanying exothermic reaction. However, the surface areas of powders calcined starting at the lower temperature are smaller (~2 m²/g) than those calcined starting at the higher temperature (~4 m²/g). It appears that the exothermic reaction may be beneficial in breaking up the powder, and we are investigating methods of controlling the reaction to produce fine powders safely.

Although we do not regularly mill the calcined powders for extended times, extended milling will break up the agglomerates. We have achieved a surface area of 7.7 m²/g for a powder milled for 24 hours with ZrO₂ balls. A micrograph of this powder is shown in Figure 1(a).

Powder Characterization. As the objective of this program is to optimize the powder synthesis technique, we do not need to perform extensive characterization on all powders. Standard tests performed on most powders include surface area determination by BET and XRD. Other tests on selected powders include SEM, DTA, ICP analysis (performed at Stanford University), carbon analysis, and tap density. We are performing the other tests recommended in the DARPA guidelines on only a few powders.

The results of characterization tests on selected powders are given in Table 3. The weight change on exposure to air at 50% relative humidity for 24 hours is ≤ 0.1%. Slightly lower weight gain is associated with higher surface area. The tap densities range from 21% to 26%. Blending the powder to reduce agglomeration does not appear to affect the tap density. Although fine powders tend to pack more loosely than coarse powders, a high tap density (26%) was achieved with the powder which was milled for 24 hours, had



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Figure 1. Micrographs of freeze-dried $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder.

- (a) Powder milled for 48 hours, surface area = $7.7 \text{ m}^2/\text{g}$.
- (b) Powder calcined at 750°C , surface area = $1.6\text{--}2 \text{ m}^2/\text{g}$,
 $T_c > 90 \text{ K}$.
- (c) Powder calcined at 825°C , surface area = $2 \text{ m}^2/\text{g}$.

Table 3
SELECTED POWDER CHARACTERIZATION

Powder	Surface Area (m ² /g)	Tap Density (%)	Weight Gain ^a (%)	XRD
DP17-42MQ ^b	7.7	26.3	0.1%	clean 1-2-3 ^f
DP17-42MQ ^c		25.3	<0.1%	clean 1-2-3 ^f
DP19-18MBQ ^d	1.76	21.0	<0.1%	clean 1-2-3 ^f
DP19-18MUQ ^e	1.04	21.0		clean 1-2-3 ^f

^a50% RH, 24 hours.

^bCalcined at 825°C, milled lightly, annealed at 890°C/550°C, milled 24 hours.

^cCalcined at 825°C, milled lightly, annealed at 890°C/550°C.

^dBlended before drying, calcined at 825°C, milled lightly, annealed at 890°C/550°C.

^eCalcined at 825°C, milled and annealed at 890°C/550°C.

^fOnly YBa₂Cu₃O_{7-δ} peaks were observed.

a high surface area, and contained few agglomerates. The high surface area of this powder and the SEM observations (Fig. 1a) indicate that the individual particles produced by the freeze-drying process are small, and agglomeration is a problem which needs to be addressed. Figure 2 shows two XRD scans performed on the same powder. The first scan was performed following the guidelines as closely as possible and the second was performed according to our normal procedure (scan conditions are given on the figure). The only significant difference is an increase in the noise level in the scan performed according to the guidelines. The powders are clean and show no evidence of extraneous phases.

Solution of Stoichiometry Problem. Various approaches were used to solve the stoichiometry problem. These approaches, described in detail in the last quarterly report, are summarized below. We are now preparing copper nitrate solutions by dissolving Cu in nitric acid. Ba acetate solutions will absorb CO₂ from the atmosphere. Ba acetate is analyzed by XRD and then added as a powder to the Cu and Y solution just before spraying. Copper and yttrium solutions are analyzed by titration methods before use. This approach results in a powder without BaCO₃ and with an analysis (ICP) of Y_{0.99}Ba_{2.02}Cu_{2.97}. Neutron diffraction analysis performed on an earlier powder at National Institute of Standards and Technology (NIST) indicated that the only impurity was CuO, a problem solved by the use of Cu and nitric acid to prepare solutions.

Critical Temperature/Critical Current Density. Critical temperature measurements are performed at Stanford University using the resistivity method rather than the susceptibility method. Figure 3 shows a resistivity/temperature plot for a sample with a T_c >90K and W <2K. The early T_c results were reported as the temperature for zero resistivity. The results reported in Table 2 which shows the effect of calcining temperature on T_c, are in accord with the recommendations. We have achieved the goal of T_c >90K and W <2K.

We are performing some measurements using a magnetometer for comparison with the resistivity measurements. Critical current density measurements are usually performed at Stanford using a magnetometer. Stanford has measured critical current density using the transport method and the magnetization method on the same sample and found the results to be similar.

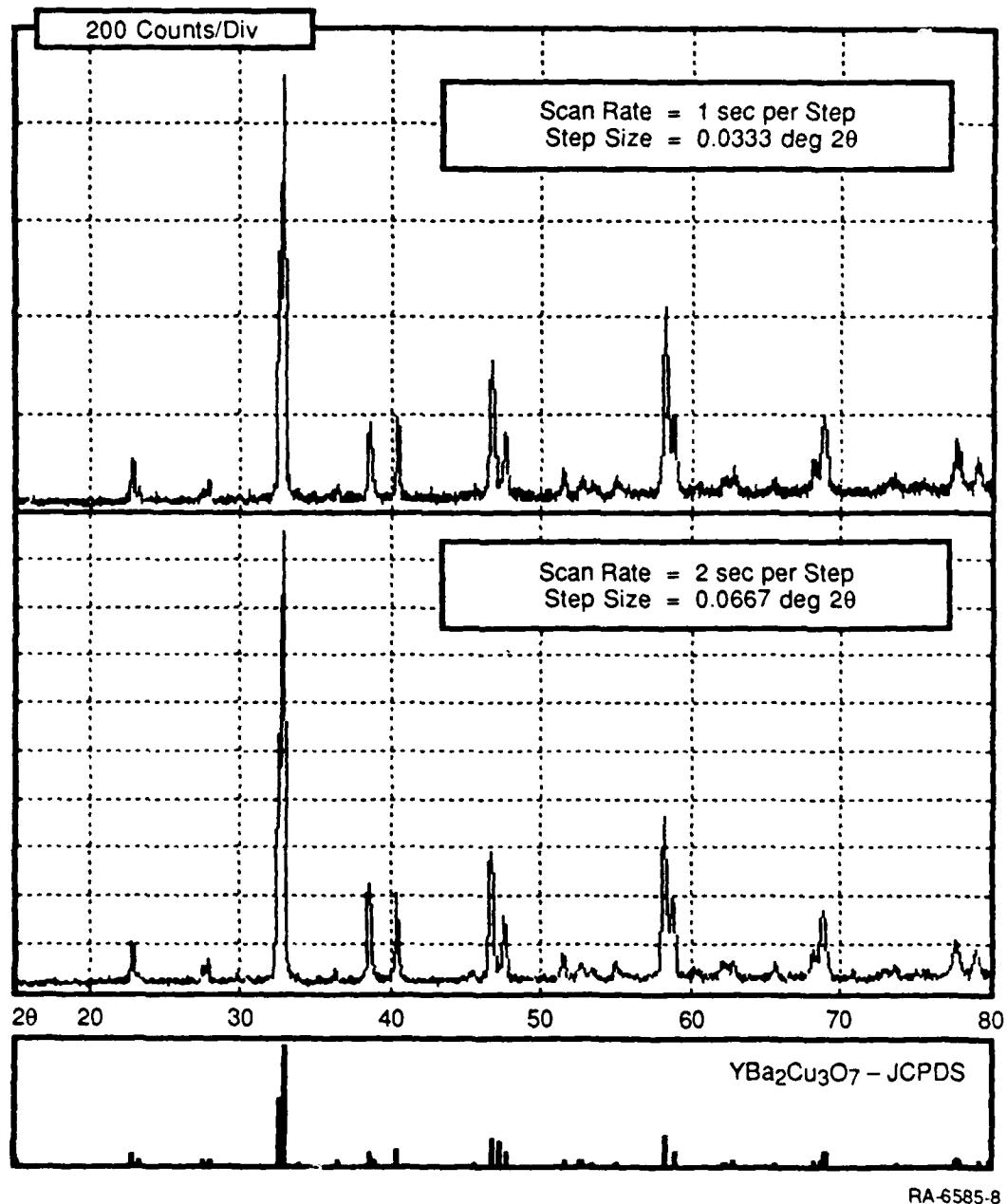


Figure 2. XRD scans of freeze-dried $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ powder.

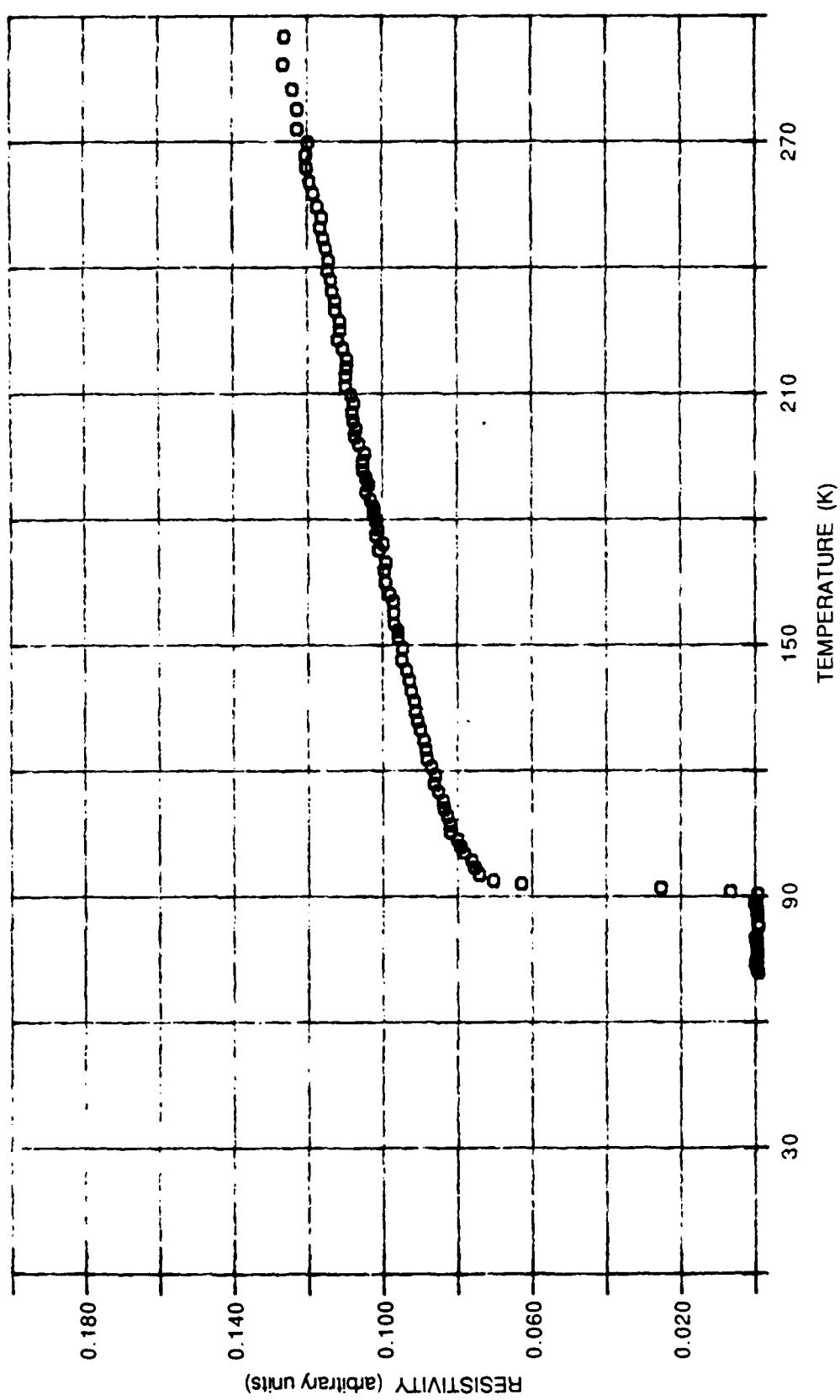


Figure 3. Resistivity-temperature plot for sample sintered from powder calcined at 750°C.

Papers Presented

"Synthesis and Processing of Superconductor Powders," S. M. Johnson and M. I. Gusman, presented at the 41st Pacific Coast Regional Meeting of the American Ceramic Society, San Francisco, October 1988.

"Synthesis of Superconductor Powders," S.M. Johnson, M. I. Gusman, L. Liu, and R. H. Lamoreaux, presented at the Annual Meeting of the American Ceramic Society, Indianapolis, April 24, 1989.

"Synthesis of Superconductor Powders by Freeze-Drying," S. M. Johnson, M. I. Gusman, L. Liu, R. H. Lamoreaux, and C-B. Eom, poster presented at MRS Spring Meeting, San Diego, April 1989.

Problem Areas

We were unable to supply powder to other researchers because we had not received the new freeze-dryer.

We are unable to measure T_c by the recommended susceptibility method because neither SRI nor Stanford University has the necessary equipment.

We have not solved the agglomeration problem, although we have made progress toward this goal.

Corrective Action

We have received the larger freeze-dryer and expect to be able to produce larger quantities of powder during the next quarter.

We would like DARPA to recommend another contractor who may be able to perform some susceptibility measurements for us.

Plans for solving the agglomeration problem were described above, and include changes in spraying procedure and pre-drying treatments.

Goals for Next Quarter

Our goals for the next quarter are to

- Continue efforts to decrease agglomeration.

- Produce larger quantities of powder and supply samples to other contractors.
- Investigate reproducibility in large batches.
- Continue investigation of calcining and freeze-drying effects on powder characteristics.
- Continue efforts to improve reproducibility of T_c data and to decrease W.

Financial Status

Funding Authorized (through March 31, 1990):	\$636,000
Funds Expended/committed (June 30, 1989):	\$268,557
Funds Required to complete the FY89:	\$140,000